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Evidence for Charge Disproportionation in (Ba,K)BiO_3 Superconductors from O 1*s* NEXAFS

M. Merz, G. Heger (RWTH Aachen, Germany), S.N. Ustinovich, S.V. Shiryaev, S.N. Barilo (Belorussian Academy of Sciences, Minsk, Belarus), N. Nücker, S. Schuppler (Forschungszentrum Karlsruhe, Germany), S. Stadler, D. Arena, J. Dvorak, Y.U. Idzerda (Naval Research Laboratory and Montana State U)

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Introduction: The $Ba_{1-x}K_xBiO_3$ family has been receiving continuous interest over many years since the compounds with x greater than a critical concentration x_c (about 0.37) are hole-doped superconductors, and the transition temperature T_c at x_c, 30 K, is among the highest ones found for non-cuprate oxides. Although the superconducting compounds are (pseudo)cubic a peculiar superstructure was recently observed along the *c* axis in highly ordered thin-film systems and along all axes in single crystals. This context provided motivation for the present, in-depth study of the electronic structure *via* polarization-dependent NEXAFS.

Methods and Materials: A large number of highly ordered thin films and high-quality single crystals was studied with polarization-dependent O 1*s* NEXAFS, effectively determining the unoccupied electronic structure of O 2*p* character close to the Fermi level, E_F, and its orbital symmetries. Due to considerable hybridization conclusions about the state of Bi in this family of compounds are possible. Fluorescence detection (FY) was utilized to ensure bulk sensitivity and low, energy-independent background.

Results: Considerable and continuous variations of the many clearly distinguishable near-edge features are observed with doping level x. In particular the lowest-lying pre-peak, a prominent feature around 529 eV called A in the following, is seen to *de*crease in intensity with increasing x, while another feature, located several eV higher in energy and called B, *in*creases almost symmetrically. This behavior of peak A is clearly unexpected since increasing x corresponds to injecting *holes* into the system, which should lead to *higher* intensity near onset. Still, the behavior can be understood straightforwardly in terms of interpreting peak A as a signature for Bi(III)-derived states and peak B as a signature for Bi(V)-derived states hybridized with O 2*p* states [1]. This interpretation, although being somewhat tentative for now, would mean that the present study provides first O 1*s* NEXAFS evidence for Bi(III)-Bi(V) charge disproportionation in this family of compounds. Some first cross-checks – like comparison to multiple-scattering calculations for related materials [2] – are consistent with this picture.

On the other hand, a recent NEXAFS study on the electronic structure and its doping dependence [3] appears to be fundamentally at variance with this: there, the lowest-lying pre-peak *in*creases in intensity with doping level x, just as our peak B does and just as expected from simple hole-concentration arguments. That study, however, used total electron yield (TEY) detection with its known complications regarding sensitivity to surface contamination etc., and while their experiments were performed impeccably (for instance, the crystals were cleaved *in situ*) one arrives, on closer inspection and by comparing to our own TEY spectra taken simultaneously to FY, at a very disturbing observation: *there is no peak corresponding to our peak A* in the spectra of Ref. [3], and the lowest-lying peak in Ref. [3] indeed seems to correspond to peak B. In our own TEY results, peak A is very small yet discernibly existent, and maybe the fairly low energy resolution used in [3] (0.7 eV as compared to 0.2 eV in the present work) also plays a role in Ref. [3] missing peak A completely.
It has been known for high-T_c oxides, for instance, that some pre-peaks when measured in TEY appear with much less than the expected spectral weight compared to the main edge – yet it seems that the present case is arguably the most striking one so far for “under-representing” an important pre-peak. We take this as a further indication for using FY instead of TEY whenever possible, and have to conclude that a reassessment of the present understanding of NEXAFS and the electronic structure of (Ba,K)BiO_3, possibly on the basis of charge disproportionation, is sorely needed.

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References:

[1] M. Merz *et al*., to be published.
[2] A. Yu. Ignatov, Nucl. Instr. Meth. A **448**, 332 (2000).
[3] K. Kobayashi *et al*., Phys. Rev. B **59**, 15100 (1999).